

Garnet–Clinopyroxene Barometry of Crustal and Mantle Assemblages: Implication for the Estimation of Diamond Potential

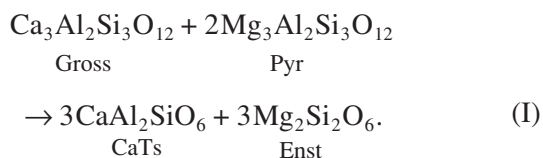
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Determination of the depth of crustal and mantle xenoliths is an urgent issue. The xenoliths are potential carriers of diamonds and subdivided into three types by composition: ultramafic, eclogite, and pyroxenite (intermediate between the two former types). Eclogites contain omphacitic clinopyroxene, while peridotites contain Cr-diopsides. This study is aimed at development of a universal garnet–clinopyroxene barometer for estimating pressure in both mantle and crustal rocks. The PT parameters can be estimated using the known effect of variation in the content of the tschermakite end member ($\text{CaAl}_2\text{SiO}_6$) in clinopyroxene with growth in pressure. The calculations were based on the model of a CaTs-tschermakite barometer [2] described by the reaction



A new thermodynamic model of Cpx was created to develop a universal barometer. It was based on the three-site model Cpx: $(\text{Fe}, \text{Ca}, \text{Na}, \text{Mg})^{\text{M2}}(\text{Fe}, \text{Mg}, \text{Cr}, \text{Al})^{\text{M1}}(\text{SiAl})^{\text{IV}}\text{Si}^{\text{IV}}\text{O}_6$ [2]. The parameters of asymmetrical interaction were taken for site M2: Fe–Ca, Ca–Fe, Mg–Ca, and Ca–Mg; Mg–Fe, Fe–Mg, Ca–Na, and Na–Ca [2]. Fe–Na and Na–Fe were taken to be equal to Mg–Na and Na–Mg. The Mg–Na and Na–Mg and Mg(Fe)–Al interactions provide the main contribution in the energetic potential of the Cpx model. Unlike the model reported in [2], interactions of Mg, Fe, and Al in site M1 were described by the following equations (J/mol):

$$W_{\text{Mg(Fe)-Al}} = -16000 + 9.65T(\text{K}), \quad (\text{I})$$

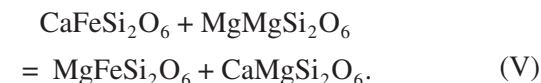
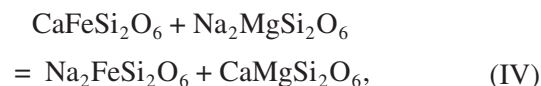
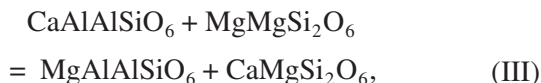
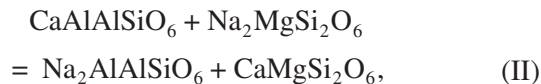
$$W_{\text{Al-Mg(Fe)}} = 135200 - 69.6T(\text{K}). \quad (\text{2})$$

The symmetrical parameters for Mg–Na and Na–Mg interaction on site M2 were taken as follows (J/mol):

$$W_{\text{Mg(Fe)-Na}} = -24000 + 1294P(\text{kbar}). \quad (\text{3})$$

In this form, they can be applied in the model of the clinopyroxene thermometer. Taking the pressure in (3) as zero, these parameters are -24 kJ/mol. Other interaction parameters were taken from [2]. Using them, the coefficients of activity of clinopyroxene end members participating in the reaction (γ_{CaTs} and γ_{CEnst}) were calculated.

It should be also taken into account for clinopyroxene that isomorphous cations are distributed over energetically nonequivalent sites M1 and M2. They interact not only within the site of a single energetic level (on M1 or M2), but also between these sites (energetic levels), ultimately providing an additional energetic contribution to the chemical potentials of minerals. This interaction is termed as cross-interaction. For clinopyroxene, this interaction is based on the following exchange reactions:



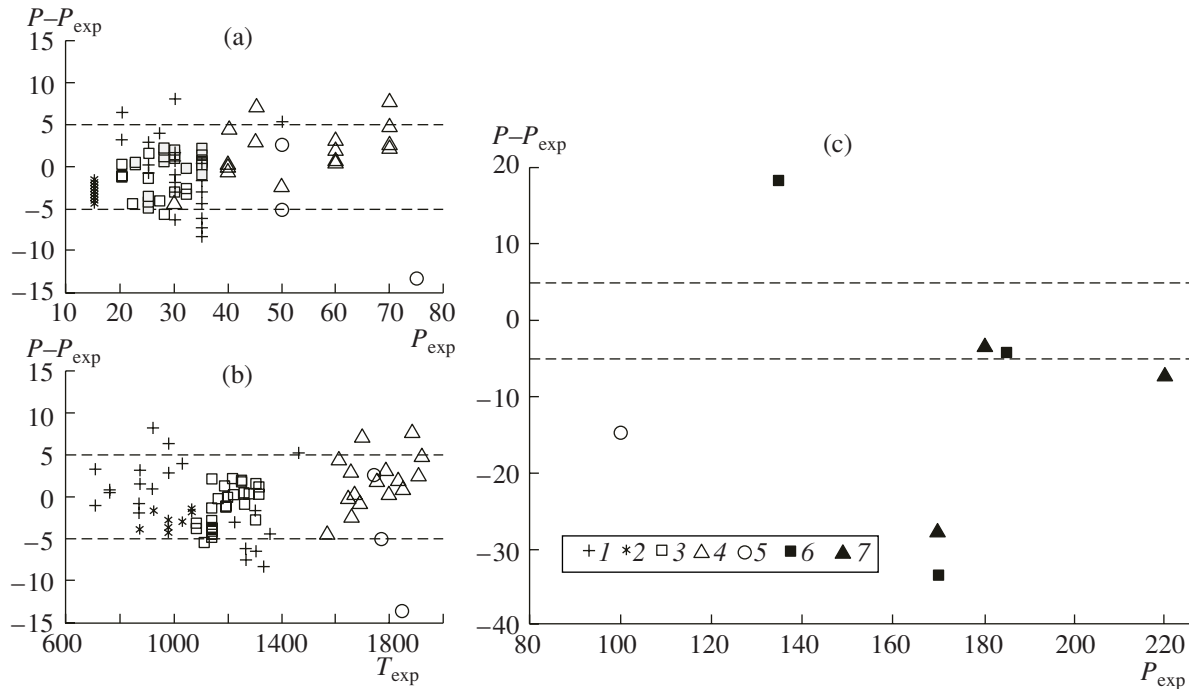


Fig. 1. Deviations of pressures calculated using our garnet–clinopyroxene barometer from experimental data on eclogite (1, 5–7) and peridotite (2–4) compositions depending on temperature and pressure. Symbols for experimental data: (1) [15], (2) [4], (3) [13], (4) [14], (5) [11], (6) [1], (7) [5].

The reactions have the following Gibbs energies: $G_{II} = -26$, $G_{III} = -0.31$, $G_{IV} = -1$, $G_V = -5.01$ (kJ/mol). Then, the additional contribution of the cross-interaction is calculated using the following expressions:

$$RT \ln \gamma_{CaTs} = (1 - Al^{M1})(Na^{M2} \Delta G_{II} + Mg^{M2} \Delta G_{III}) - Fe^{M1}(Na^{M2} \Delta G_{IV} + Mg^{M2} \Delta G_V), \quad (4)$$

$$RT \ln \gamma_{CEnst} = (1 - Mg^{M2})(Al^{M1} \Delta G_{III}^+ Fe^{M1} \Delta G_V) - Na^{M2}(Al^{M1} \Delta G_{II}^+ + Fe^{M1} \Delta G_{IV}). \quad (5)$$

The proposed model can be used both for omphacites and for diopsides.

The activity of clinopyroxene end members is calculated using the following equations:

$$\alpha_{CEn} = \gamma_{CEn} Mg^{M2} Mg^{M1} (Si)^2, \quad (6)$$

$$\alpha_{CaTs} = \gamma_{CaTs} 4Ca^{M2} Al^{M1} Al^{IV} Si, \quad (7)$$

where $Si = X_{Si}/2$.

The temperature dependence of the Gibbs energy for reaction (I), molar volumes of end members in the clinopyroxene and garnet solutions, and activities of grossular and pyrope were calculated according to [2]. In addition, the proposed version recalculates the initial pressures of more than 60 kbar with the introduction of a correction for temperature- and pressure-dependent expansibility and compressibility.

The proposed version of a geobarometer makes it possible to calculate the pressure for peridotite, eclogite, and granulite experiments in the garnet–clinopyroxene system within the ranges of $700^\circ \leq T \leq 1800^\circ C$ and $15 \leq P \leq 75$ Kbar (85 analyses) with accuracy $1\sigma = 4$ kbar and Δ (average) = 3 kbar (Fig. 1a). The use of this barometer for known eclogite experiments at 100–220 kbar and 1500–2100°C shows significantly lower accuracy [1, 5], and the error can be as much as 30–40% (Fig. 1b). Nonetheless, this barometry gives an approximate estimate of the depth of these assemblages.

Using this barometer, we calculated the *PT* parameters for known eclogite inclusions in diamonds, diamond–graphite, barren eclogites, websterites from the well-known pipes in South Africa, and granulites of the Adirondack metamorphic complex (Fig. 2). These calculations indicate that inclusions in the diamonds and diamondiferous xenoliths were formed within the diamond stability field, whereas barren rocks are plotted in the graphite stability field. The highest *PT* parameters (70–90 kbar) were obtained for the diamond inclusions from the Monastery pipe, while the Adirondack granulites were formed at the lowest pressure (5–10 kbar) (Fig. 2). This barometer was also used to estimate *PT* conditions of the eclogitic assemblages in the garnet–clinopyroxene system from kimberlites of Venezuela, diamondiferous eclogites of the Udachnaya pipe, and barren eclogites

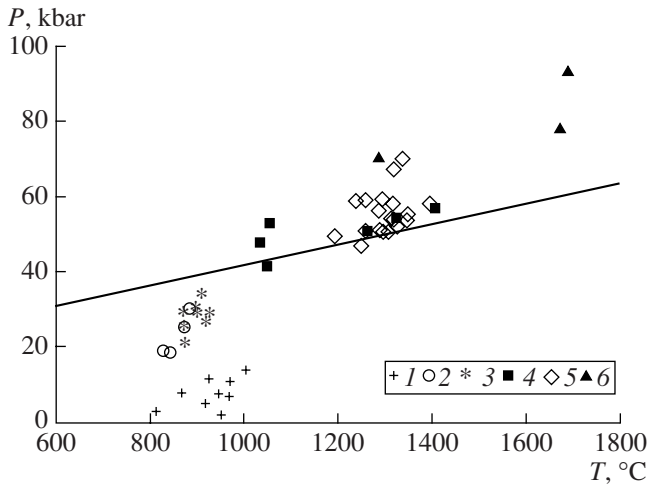


Fig. 2. Temperatures and pressures calculated for granulites of the Adirondack metamorphic complex (1), garnet websterites from the Lesotho pipe (2), eclogites from the Lesotho pipes (3), diamondiferous garnet eclogites from the Orapa pipe (4), and eclogite inclusions in diamonds of the Premier (5) and Monastery pipes (6) relative to the graphite–diamond equilibrium line (analyses were taken from [6–10]).

of the Obnazhennaya pipe. Pressures based on diamonds are within 50–70 kbar, which is consistent with the pressure estimates based on the coesite barometer [12]. The diamondiferous xenoliths of the Udachnaya pipe have PT parameters corresponding to the diamond stability field, whereas eclogites from the barren Obnazhennaya pipe correspond to the graphite stability field (Fig. 3).

The results obtained indicate that the developed model of the garnet–clinopyroxene barometer can be applied to estimate depths of the crustal, mantle, and superdeep mantle assemblages. This model fits the required petrological criteria and can be applied for elucidating the diamond potential of mantle and crustal assemblages.

ACKNOWLEDGMENTS

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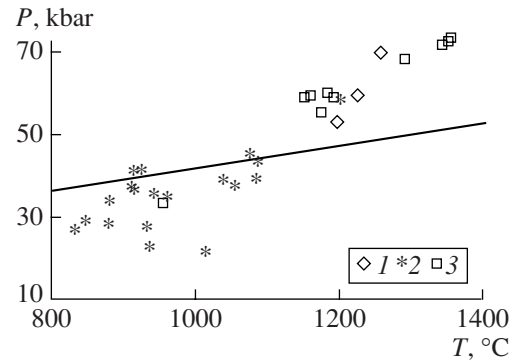


Fig. 3. Temperatures and pressures calculated for garnet–clinopyroxene assemblages from eclogite xenoliths of the Obnazhennaya (1) and Udachnaya (2) pipes and Venezuela diamonds (3) relative to the graphite–diamond equilibrium line (analyses were taken from [3, 12]).

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